

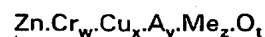
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(54) **Catalyst and its use for  
producing methanol/higher alcohol  
mixtures**

(57) There is disclosed a catalyst, and process, for producing mixtures of methanol and higher alcohols from synthesis gas, the catalyst comprising zinc, chromium, copper, one or more alkaline metals, and possibly one or more other metals chosen from molybdenum, manganese, lanthanum, cerium, aluminium,

titanium and vanadium, either all or only part of said elements being chemically bonded to oxygen and/or to each other. The catalyst has the empirical formula:



in which w is 0.1—0.8, x is 0.005—0.05, y is 0.002—0.2, z is 0—0.1 and t is 3.75—1.2, A being the alkaline metal and Me being the other metal.

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## SPECIFICATION

## Catalyst and its use for producing methanol/higher alcohol mixtures

This invention relates to a catalyst and its use in the production of mixtures of methanol and higher alcohols from  $H_2$  and CO, possibly in the presence of  $CO_2$  and inerts.

5 The above mixtures are useful in particular as petrol substitutes, and can also be mixed therewith in various percentages for use as fuels for internal combustion engines. 5

Many catalysts are known for the production of methanol in mixture with higher alcohols. "Catalysis", Brimet (Vol 5) describes among others a catalyst comprising Cu, ZnO and  $Cr_2O_3$  in the molar proportions of 82%, 16% and 2% respectively.  $K_2O$  must be added to these components to give the necessary selective activity. A further catalyst described in this document is prepared from  $Zn(OH)_2$ , 10  $Cu(OH)_2$  and  $K_3[Cr(CO)_4] \cdot 3H_2O$  in equimolar mixture. 10

Canadian Patent No. 273,984 describes a catalyst composed of one or more metal oxides chosen from Ag, Cu, Zn, Mn, Mo, U and V, and one or more alkaline or alkaline earth oxides, in which the number of atoms of the alkaline metal oxides must be equal to one half the total number of atoms of the other metals. Finally, French Patent No. 2,369,234 describes a catalyst composed of Cu, Co at least one 15 element chosen from Cr, Fe, V and Mn, and at least one alkaline metal, the composition range being fairly wide. 15

With all these types of catalyst, the productivity and selectivity obtained in producing methanol and higher alcohols are not very high. In addition, these catalysts age rapidly, consequently losing both 20 activity and selectivity. In addition to these drawbacks, it is known that beyond a certain temperature ( $300^\circ C$ ), catalysts which contain copper cannot be used because of methanation. 20

According to the present invention, there is provided a catalyst for use in producing mixtures of methanol and higher alcohols from a gas comprising CO and  $H_2$ , the catalyst comprising the elements zinc, chromium, copper, one or more alkaline metals and optionally one or more other metals, said 25 elements being chemically bonded, at least in part, to oxygen and/or to each other, the catalyst having the following empirical formula:  $Zn.Cr_w.Cu_x.A_y.Me_z.O_t$  in which w is from 0.1 to 0.8, x is from 0.005 to 0.05, y is from 0.002 to 0.2, z is from 0 to 0.1, t is from 3.75 to 1.3 (its value being that necessary for satisfying the valency with which the various elements are present in the catalyst), A is the alkaline 30 metal or metals, and Me is the other metal or metals optionally present. 25

The catalyst usually gives both better productivity and selectivity than normally used catalysts. In addition, it usually has long stability with time. The use of such a catalyst in place of conventionally used catalysts leads to reduced methanation, while the methanol synthesis takes place at a sufficiently high 30 rate, and the hydrogenation of the intermediates leads to more stable products. 30

The catalyst according to the present invention comprises the following elements: zinc, chromium, 35 copper, one or more alkaline metals (e.g. alkali metals or alkaline earth metals, potassium being preferred), and possibly one or more other metals (for example molybdenum, manganese, lanthanum, cerium, aluminium, titanium and vanadium). 35

In preferred embodiments, w is from 0.3 to 0.6, and/or x is from 0.01 to 0.03, and/or y is from 0.01 to 0.1, and/or z is from 0 to 0.4.

40 The present invention also provides a process for producing a mixture of methanol and higher alcohols, which process comprises contacting a gas comprising CO and  $H_2$  with a catalyst according to the invention. 40

In a preferred embodiment, the process comprises feeding the reaction zone, containing the aforesaid catalyst, with  $H_2$ , CO and possibly  $CO_2$  and inerts in a molar  $H_2:CO$  ratio of from 0.2:1 to 10:1 45 preferably from 0.5:1 to 3:1, at a temperature within the range of  $330^\circ$  to  $460^\circ C$ , preferably  $360^\circ$  to  $440^\circ C$ , at a pressure of from 2000 to 30000 KPa, preferably from 6000 to 18000 KPa, and at a spacial velocity of from 5000 to 30000 GHSV, preferably from 5000 to 15000 GHSV. 45

The gaseous mixture used for the alcohol formation reaction can be synthesis gas obtained, for example, by the partial combustion of coal, natural gas or hydrocarbons. The process may be carried out 50 by bringing the gaseous mixture into contact with the catalyst in a suitable reactor, which can either be of the fluid or fixed bed type. The temperature, pressure and spacial velocity may be the most convenient for the catalyst used, and are preferably within the range of the aforesaid values. 50

The catalyst can be prepared by various methods, of which the following are described in particular. One of the methods comprises adding an alkaline carbonate to an aqueous solution 55 containing salts of zinc, chromium, copper and optionally the element or elements Me in order to obtain a precipitate which is then separated, dried, calcined, fed with the alkaline element, reduced and possibly moulded into the size suitable for the chosen catalytic bed. The second of these methods comprises reacting zinc oxide with mixtures of ammonium dichromate and alkaline metal dichromates in a ratio such that the final catalyst contains the required quantity of alkaline oxides. The copper and, if 60 required, the element Me can be added by final impregnation of the already formed catalyst, using a soluble salt such as nitrate, carbonate, acetate, formate or other organic salt. This is followed by calcining to decompose the salt and to eliminate the anion by evaporation. 60

The catalyst may be reduced either before or after introducing the alkaline metals. The reducing gas is preferably hydrogen or a synthesis gas, preferably diluted with an inert gas such as nitrogen. The

gradually rising temperature in the catalyst bed is preferably controlled in such a manner that it does not exceed 350°C at the end.

- The catalyst can be supported or unsupported. Preferred supports are inert materials of low surface area such as alpha alumina, corundum, mellite, cordierite and silica. The support can be added either during the catalyst preparation in the precipitation stage or in the final stage by mechanical mixing during pellet formation, extrusion, etc.

The following Examples 1 to 7 and 9 to 16 illustrate the invention.

#### EXAMPLE 1

- This Example describes the preparation of a catalyst having the following composition, in terms of its base elements:  $\text{Zn.Cr}_{0.35}\text{.Cu}_{0.027}\text{.K}_{0.02}$

- To prepare this catalyst, 59 g of chromic anhydride were dissolved in deionised water so as to produce a 30% by weight solution of  $\text{CrO}_3$ . An aqueous suspension of 140 g of zinc oxide in 2 litres of deionised water was prepared separately. The chromic solution was added to this suspension, which was kept under strong stirring, and stirring was continued for some hours to ensure complete homogenisation. The precipitate was filtered off, taken up with water, dried by atomisation, and pelletised.

- The pellets were impregnated with an aqueous ammoniacal solution of copper acetate and potassium acetate prepared by dissolving 3.8 g of potassium acetate in 3 cc of water, adding 11 cc of 32% ammonia solution followed by 9.3 g of copper acetate, and stirring the mixture until the copper acetate had completely dissolved.

- The already prepared pellets were then impregnated. They were dried at 110°C in an oven for eight hours, and then calcined at 280°C for eight hours. The catalyst was reduced by placing 20 cc of pellets in a copper-clad stainless steel tubular reactor immersed in a bath of fluidised sand, and heated to about 300°C in a nitrogen stream containing about 2% of hydrogen. During the reduction, the hydrogen flow was controlled so that the temperature did not exceed 350°C. Reduction was complete in about 24 hours.

The catalyst prepared in this manner was ready for use in the synthesis of methanol and higher alcohols.

#### EXAMPLE 2

- This Example describes the preparation of a catalyst having the following composition, in terms of base elements:  $\text{Zn.Cr}_{0.33}\text{.Cu}_{0.018}\text{.K}_{0.023}$

- To prepare this catalyst, 1 g of cupric nitrate and 30 g of chromium nitrate were dissolved in 500 cc of deionised water, by heating and stirring vigorously. 18.5 g of zinc oxide were suspended in 500 cc of deionised water. The first solution was poured into the zinc oxide suspension, the mixture then being heated under stirring to 90°C. A quantity of a solution prepared by dissolving 50 g of  $\text{K}_2\text{CO}_3$  in 500 cc of deionised water was then added so as to raise the pH to 9. After one hour the mixture was cooled, neutralised to pH 7 with a 15% solution of nitric acid, and the precipitate was filtered off and washed repeatedly with water. The precipitate was dried at 110°C for four hours. The potassium content was determined and found to be 0.8% by weight. Pelletising was then carried out to obtain a catalyst, by the procedure described in Example 1.

#### EXAMPLE 3

This Example describes the preparation of a catalyst having the following composition, in terms of its base elements:  $\text{Zn.Cr}_{0.33}\text{.Cu}_{0.018}\text{.Na}_{0.06}$

- The procedure described in Example 2 was followed, but using an  $\text{Na}_2\text{CO}_3$  solution prepared by dissolving 80 g of  $\text{Na}_2\text{CO}_3$  in a litre of water, instead of the  $\text{K}_2\text{CO}_3$  solution. On analysis, the Na content was found to be 1.27%.

#### EXAMPLE 4

This Example describes the preparation of a catalyst having the following composition in terms of its base elements:  $\text{Zn.Cr}_{0.35}\text{.Cu}_{0.027}\text{.K}_{0.023}\text{.Mn}_{0.04}$

- The catalyst was prepared by the procedure described in Example 1, but by additionally adding 17.9 g of manganese acetate to the final impregnating solution.

#### EXAMPLE 5

This Example describes the preparation of a catalyst having the following composition, in terms of the base elements:  $\text{Zn.Cr}_{0.35}\text{.Cu}_{0.027}\text{.K}_{0.023}\text{.Al}_{0.082}$

- The procedure described in Example 1 was followed, but 55.72 g of aluminium nitrate were additionally added to the final impregnating solution.

#### EXAMPLE 6

This Example describes the preparation of a catalyst having the following composition, in terms of its base elements:  $\text{Zn.Cr}_{0.4}\text{.Cu}_{0.028}\text{.K}_{0.023}$

The procedure described in Example 1 was followed, but using 66 g of chromic anhydride and 132 g of zinc oxide instead of the quantities stated in Example 1.

#### EXAMPLE 7

This Example describes the preparation of a catalyst having the following composition, in terms of its base elements:  $\text{Zn.Cr}_{0.45}.\text{Cu}_{0.029}.\text{K}_{0.02}$ .

The procedure described in Example 1 was followed, but using 90 g of chromic anhydride, 162 g of zinc oxide, 11.7 g of copper acetate and 3.4 g of potassium acetate.

#### EXAMPLE 8 (Comparison)

This Example describes the preparation of a catalyst having the following composition, in terms of its base elements:  $\text{Zn.Cr}_{0.35}.\text{K}_{0.02}$ .

This catalyst was prepared for comparison purposes. The preparation was carried out as described in Example 1, but without adding the copper salt to the final impregnation solution.

#### EXAMPLES 9—15

The catalysts prepared and activated as described in Examples 1 to 7 were tested for the synthesis of methanol and higher alcohols. A synthesis gas consisting of 66—69% of  $\text{H}_2$ , 30—33% of  $\text{CO}$ , 0—3% of  $\text{CO}_2$ , 0.1% of  $\text{CH}_4$  and 0.3% of  $\text{N}_2$  was used.

The liquid reaction product was separated by cooling and condensation. Average samples collected after about 24 hours of test operation were analysed by gas chromatography. The reaction conditions (pressure, temperature, spacial velocity) and the results obtained, are given in Table 1.

#### EXAMPLE 16

A life test lasting more than 435 hours was carried out using the catalyst prepared as in Example 1. Thus, 35 cc of catalyst were placed in a tubular reactor. A synthesis gas mixture whose composition was kept within the range of values given in Example 15 was fed through the reactor at a throughput of about 10,000 GHSV. The average reaction temperature was  $400^\circ\text{C} \pm 5^\circ\text{C}$ , and the operating pressure was 13,000 KPa. The results are given in Table 2. These show that there was no substantial variation in productivity or selectivity with time.

#### EXAMPLE 17 (comparison)

A life test was carried out on the comparison catalyst prepared as in Example 8, operating under the same reaction conditions as described in Example 16. The results are given in Table 3. These show that this catalyst degenerates with time both in terms of productivity and selectivity, and in addition is much less active from the beginning.

TABLE 1

Example		9					
Catalyst		(Catalyst as in Example 1)					
Pressure	KPa	9,000	13,000	16,000	13,000	13,000	13,000
Temperature	°C	398 — 404	397 — 404	397 — 404	398 — 403	398 — 404	416 — 421
GHSV	h <sup>-1</sup>	10,650	11,400	10,340	15,030	6,870	10,650
Methanol	% wt.	57.7	61.5	68.2	66.2	54	53.2
Ethanol	"	1.9	1.6	1.3	1.4	1.8	2.3
n-propanol	"	1.5	1.7	1.4	1.6	1.8	1.8
i-butanol	"	18.1	15.8	13.6	15	19.5	21.6
Higher alcohols	"	21.5	19.3	15.5	15.5	22.5	21
(C ≥ 5)							

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TABLE 1 (Continued)

Example		10	11	12
Catalyst		(Cat. Ex. 2)	(Cat. Ex. 3)	(Cat. Ex. 4)
Pressure	KPa	13,000	13,000	13,000
Temperature	°C	392 – 405	398 – 400	397 – 402
GHSV	h <sup>-1</sup>	9,560	10,200	11,170
Methanol	% wt.	71.4	78.6	67.6
Ethanol	„	1.8	1.4	2.1
n-propanol	„	1.5	1.9	3.7
i-butanol	„	9.7	8.7	14.8
Higher alcohols (C ≥ 5)	„	15.6	7.8	11.8

TABLE 1 (Continued)

Example		13	14	15
Catalyst		(Cat. Ex. 5)	(Cat. Ex. 6)	(Cat. Ex. 7)
Pressure	KPa	13,000	13,000	13,000
Temperature	°C	399 – 403	398 – 401	396 – 400
GHSV	h <sup>-1</sup>	11,400	11,800	10,200
Methanol	% wt.	79.2	69.6	57.3
Ethanol	„	1.3	1.8	1.9
n-propanol	„	1.9	2.3	2.8
i-butanol	„	8.7	14.9	16.6
Higher alcohols (C ≥ 5)	„	8.8	11.4	21.4

TABLE 2

Catalyst	(Catalyst as in Example 1)				
	47	95	204	326	449
Hours of operation					
Productivity g/hl	586	553	586	548	552
Methanol % wt.	64	67	63.6	61.5	64.6
Ethanol "	1.7	2	1.7	1.6	2.3
n-propanol "	1.6	1.7	1.7	1.7	2.2
i-butanol "	16.8	14	16.1	15.8	16.9
Higher alcohols " (C $\geq$ 5)	15.8	15.2	16.8	12.3	14

TABLE 3

Catalyst	(Catalyst as in Example 8)				
	40	100	245	303	384
Hours of operation					
Productivity g/hl	493	485	448	414	357
Methanol % wt.	80.6	82.2	83.5	84.3	85.1
Ethanol "	2.3	2.5	2.6	2.7	2.8
n-propanol "	4.7	5	5.2	5	4.7
i-butanol "	10.5	8.7	7.6	7	6.4
Higher alcohols " (C $\geq$ 5)	2	1.5	1.1	0.4	1

## CLAIMS

1. A catalyst for use in producing mixtures of methanol and higher alcohols from a gas comprising CO and H<sub>2</sub>, the catalyst comprising the elements zinc, chromium, copper, one or more alkaline metals and optionally one or more other metals, said elements being chemically bonded, at least in part, to oxygen and/or to each other, the catalyst having the following empirical formula:  $Zn.Cr_w.Cu_x.A_y.Me_z.O_t$  in which w is from 0.1 to 0.8, x is from 0.005 to 0.05, y is from 0.002 to 0.2, z is from 0 to 0.1, t is from 3.75 and 1.3 (its value being that necessary for satisfying the valency with which the various elements are present in the catalyst), A is the alkaline metal or metals, and Me is the other metal or metals optionally present. 5
2. A catalyst as claimed in claim 1 or 2, wherein w is from 0.3 to 0.6, x is from 0.01 to 0.03, y is from 0.01 to 0.1, and z is from 0 to 0.04. 10
3. A catalyst as claimed in claim 1 or 2, wherein the other metal or metals is or are chosen from molybdenum, manganese, lanthanum, cerium, aluminium, titanium and vanadium.
4. A catalyst as claimed in any of claims 1 to 3, wherein the alkaline metal is potassium.
5. A catalyst as claimed in claim 1, substantially as described in any of the foregoing Examples 1 to 7. 15
6. A process for producing a mixture of methanol and higher alcohols, which process comprises contacting a gas comprising CO and H<sub>2</sub> with a catalyst as claimed in any of claims 1 to 5.
7. A process according to claim 6, wherein the H<sub>2</sub>:CO molar ratio of the gas is from 0.2:1 to 10:1.
8. A process according to claim 7, wherein the H<sub>2</sub>:CO molar ratio of the gas is from 0.5:1 to 3:1. 20
9. A process according to any of claims 6 to 8, wherein the temperature is from 330 to 460°C.
10. A process according to claim 9, wherein the temperature is from 360 to 440°C.
11. A process according to any of claims 6 to 10, wherein the pressure is from 2000 to 30000 KPa.
12. A process according to claim 11, wherein the pressure is from 6000 to 18000 KPa. 25
13. A process according to any of claims 6 to 12, wherein the spacial velocity is from 5000 to 30000 GHSV.
14. A process according to claim 13, wherein the spacial velocity is from 5000 to 15000 GHSV.
15. A process according to any of claims 6 to 14, wherein the gas further comprises CO<sub>2</sub> and/or inert gas. 30
16. A process according to claim 6, substantially as described in any of the foregoing Examples 9 to 16.
17. A mixture of methanol and higher alcohols, produced by a process according to any of claims 6 to 16.

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